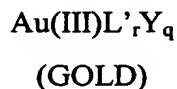


**We Claim:**

1. A photothermographic material comprising a support and having on at least one side thereof, one or more imaging layers comprising a binder and in reactive association:

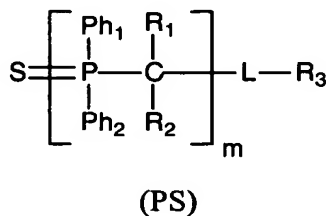
- a. photosensitive silver halide grains,
  - b. a non-photosensitive source of reducible silver ions, and
  - c. a reducing composition for said reducible silver ions,
- wherein said photosensitive silver halide grains have been chemically sensitized with a combination of chemical sensitizers that consists essentially of:

1) a gold (III)-containing compound that is represented by the following Structure GOLD:



wherein L' represents the same or different ligands, each ligand comprising at least one heteroatom that is capable of forming a bond with gold, Y is an anion, r is an integer of from 1 to 8, and q is an integer of from 0 to 3, and

2) a sulfur-containing compound that is a diphenylphosphine sulfide that is represented by the following Structure PS:



wherein Ph<sub>1</sub> and Ph<sub>2</sub> are the same or different phenyl groups, R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an alkyl or phenyl group, L is a direct bond or a linking group, m is 1 or 2 and when m is 1, R<sub>3</sub> is a monovalent group, and when m is 2, R<sub>3</sub> is a divalent aliphatic linking group having 1 to 20 carbon, nitrogen, oxygen, or sulfur atoms in the chain, and

the molar ratio of said gold(III)-containing compound to said sulfur-containing compound used in the chemical sensitization is at least 1:1.

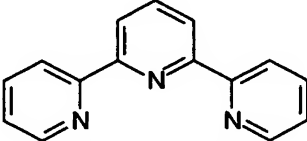
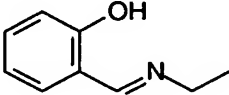
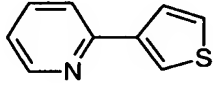
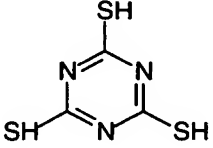
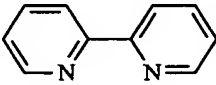
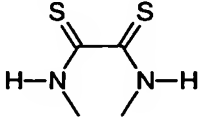
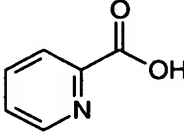
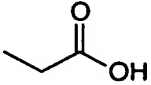
2. The photothermographic material of claim 1 wherein said  
5 one or more imaging layers further comprise a phosphor that is sensitive to X-radiation and is present in an amount of at least 0.1 mole per mole of total silver and the total silver present in said photothermographic material is at least 0.002 mol/m<sup>2</sup>.

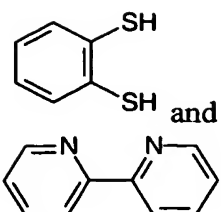
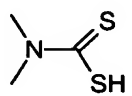
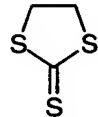
10 3. The photothermographic material of claim 1 wherein said silver halide is chemically sensitized with said gold(III)-containing compound in an amount of from about 10<sup>-8</sup> to about 10<sup>-2</sup> mole per mole of total silver and with said sulfur-containing compound in an amount of from about 10<sup>-6</sup> to about 10<sup>-1</sup> mole per mole of total silver .

15 4. The photothermographic material of claim 1 wherein L' represents the same or different ligands that comprise at least one oxygen, nitrogen, sulfur, or phosphorous atom.

20 5. The photothermographic material of claim 4 wherein L' is pyridine, bipyridine, terpyridine, P(phenyl)<sub>3</sub>, carboxylate, imine, phenol, mercaptophenol, imidazole, triazole, and dithiooxamide, Y is a halide, r is an integer of from 1 to 3, and q is 3.

25 6. The photothermographic material of claim 1 wherein said gold(III)-containing compound is one or more of Compounds Au-1 to Au-14.

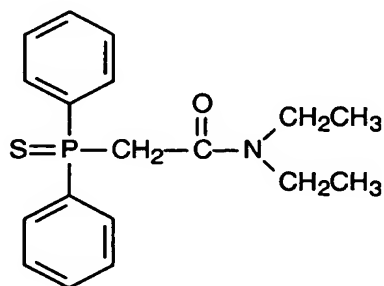
Compound	Au(III) Complex	Ligand-H (L'-H)
(Au-1)	AuL'ClBr <sub>2</sub>	P(phenyl) <sub>3</sub>
(Au-2)	AuL'Cl <sub>3</sub>	 <p>Terpyridine</p>
(Au-3)	AuL'Br <sub>2</sub>	
(Au-4)	AuL'Cl <sub>3</sub>	
(Au-5)	L'[AuP(phenyl) <sub>3</sub> ] <sub>3</sub>	
(Au-6)	AuL'Cl <sub>3</sub>	
(Au-7)	AuH(L') <sub>2</sub> Cl <sub>2</sub>	
(Au-8)	AuL'Cl <sub>2</sub>	
(Au-9)	Au <sub>2</sub> Zn(L') <sub>8</sub>	

(Au-10)	$\text{AuPF}_6(\text{L}')_2$	 <chem>SSC1=CC=CC=C1</chem> and <chem>c1ccc2nc3ccccc3nc2c1</chem>
(Au-11)	$\text{Au}(\text{L}')_2\text{Br}$	 <chem>CN(C)C(S)=S</chem>
(Au-12)	$\text{AuL}'\text{Cl}_3$	 <chem>S1CC(S)SC1=S</chem>
(Au-13)	$\text{Au}(\text{L}')_2(\text{ClO}_4)_3$	Diferrocenylphenylphosphine
(Au-14)	$\text{AuL}'\text{Cl}$	Glycylglycyl-L-histidine

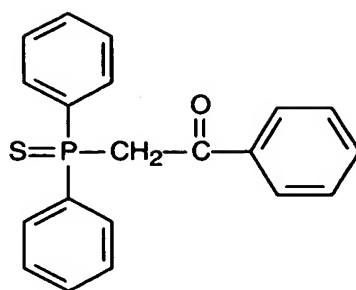
7. The photothermographic material of claim 1 wherein  $\text{R}_1$  and  $\text{R}_2$  are both hydrogen or one of them is methyl, L is a direct bond or sulfonyl or carbonyl linking group, m is 1 and  $\text{R}_3$  is an alkyl, aryl, or dialkylamino group.

8. The photothermographic material of claim 1 wherein said sulfur-containing compound is one or more of the following diphenylphosphine sulfide compounds PS-1 to PS-19:

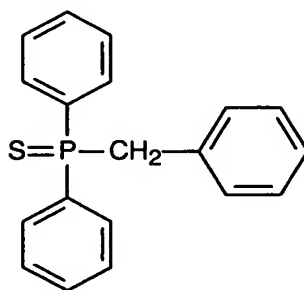
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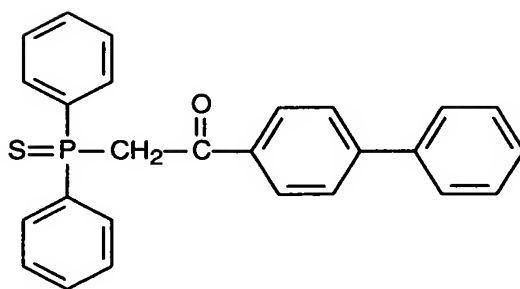
(PS-1)



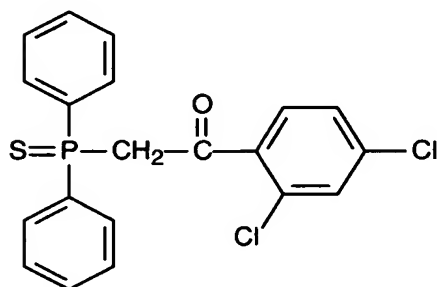
(PS-2)



(PS-3)



(PS-4)

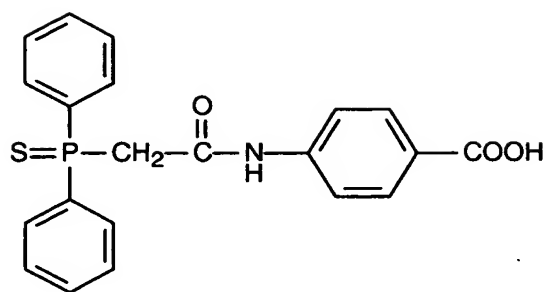


(PS-5)

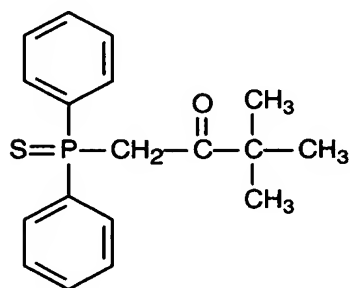
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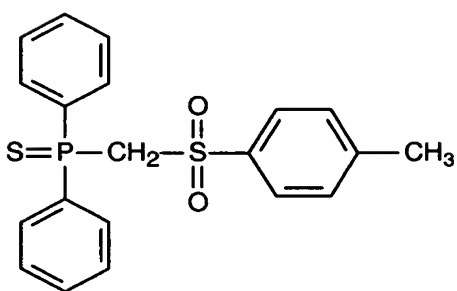
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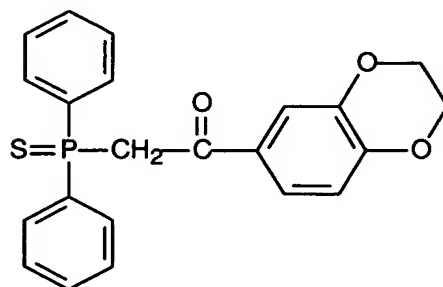
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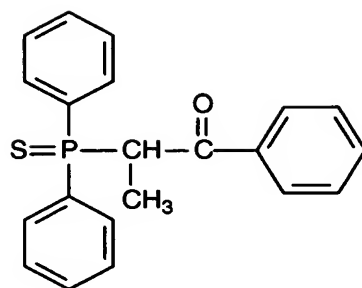
(PS-7)



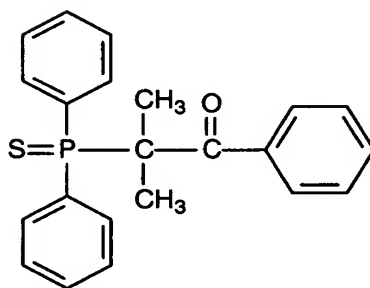
(PS-8)



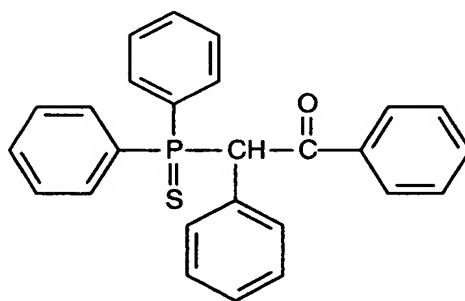
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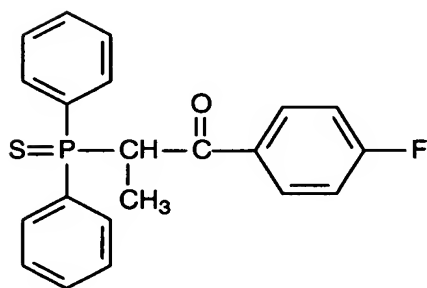
(PS-10)



(PS-11)



(PS-12)

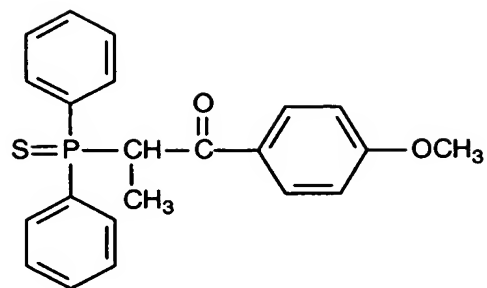


(PS-13)

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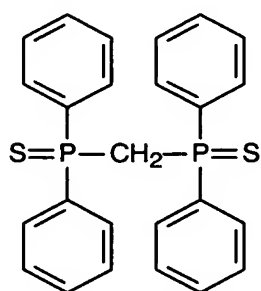
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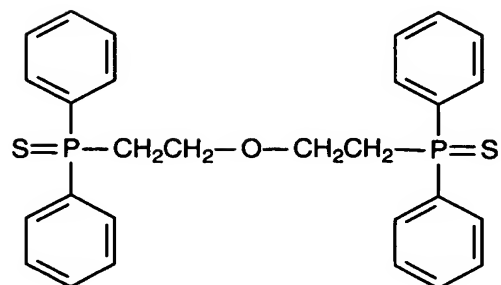


(PS-14)

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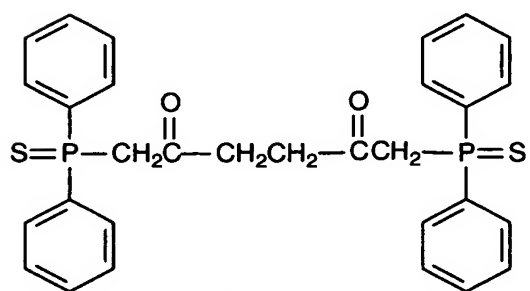


(PS-15)



(PS-16)

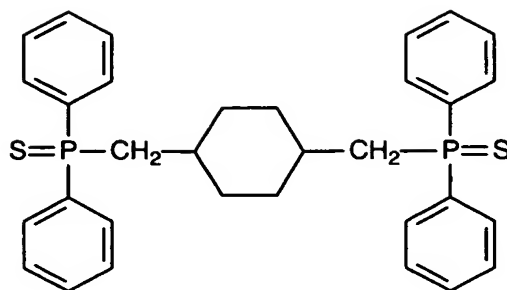
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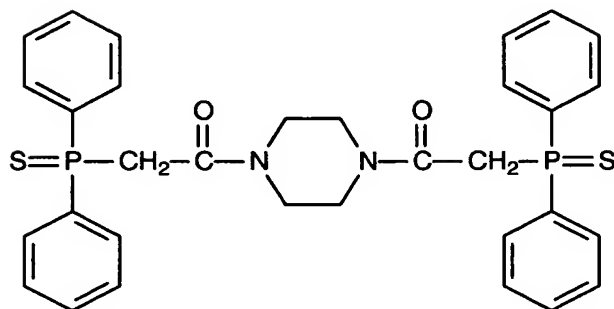
(PS-17)

15





(PS-18)



(PS-19).

5

9. The photothermographic material of claim 1 wherein said  
photosensitive silver halide has been chemically sensitized by decomposition of  
10 said sulfur-containing compound on or around the grains thereof in an oxidizing  
environment.

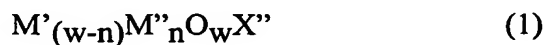
10. The photothermographic material of claim 1 wherein said  
binder is a hydrophobic binder or a polymeric latex binder, and said  
15 non-photosensitive source of reducible silver ions is a silver salt of a fatty acid  
having from 10 to 30 carbon atoms, or a mixture of said silver salts, at least one of  
which is silver behenate.

11. The photothermographic material of claim 1 wherein said  
20 photosensitive silver halide is chemically sensitized with a mixture of gold-  
containing compounds, at least 50 mol % of which are gold(III)-containing  
compounds represented by Structure GOLD.

12. The photothermographic material of claim 1 wherein said photosensitive silver halide is further chemically sensitized with a second sulfur-containing compound other than a Structure PS compound, a tellurium-containing  
5 compound, a selenium-containing compound, or a mixture of any of these compounds.

13. The photothermographic material of claim 1 further comprising in one or more of said imaging layers a phosphor that is calcium  
10 tungstate ( $\text{CaWO}_4$ ), an activated or unactivated lithium stannate, a niobium and/or rare earth activated or unactivated yttrium, lutetium, or gadolinium tantalates, a rare earth-activated or unactivated middle chalcogen phosphor, or a terbium-activated or unactivated lanthanum and lutetium middle chalcogen phosphor.

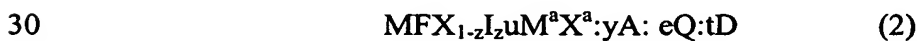
14. The photothermographic material of claim 1 further comprising a phosphor that is a rare earth oxychalcogenide and halide phosphor represented by the following formula (1):



wherein  $\text{M}'$  is at least one of the metals yttrium (Y), lanthanum (La), gadolinium  
20 (Gd), or lutetium (Lu),  $\text{M}''$  is at least one of the rare earth metals dysprosium (Dy), erbium (Er), europium (Eu), holmium (Ho), neodymium (Nd), praseodymium (Pr), samarium (Sm), tantalum (Ta), terbium (Tb), thulium (Tm), or ytterbium (Yb),  $\text{X}''$  is a middle chalcogen (S, Se, or Te) or halogen,  $n$  is 0.002 to 0.2, and  $w$  is 1 when  $\text{X}''$  is halogen or 2 when  $\text{X}''$  is a middle chalcogen.

25

15. The photothermographic material of claim 1 further comprising a phosphor that is the product of firing starting materials comprising optional oxide and a combination of species characterized by the following formula (2):



30

wherein “M” is magnesium (Mg), calcium (Ca), strontium (Sr), or barium (Ba), “F” is fluoride, “X” is chloride (Cl) or bromide (Br), “I” is iodide, M<sup>a</sup> is sodium (Na), potassium (K), rubidium (Rb), or cesium (Cs), X<sup>a</sup> is fluoride (F), chloride (Cl), bromide (Br), or iodide (I), “A” is europium (Eu), cerium (Ce), samarium (Sm), or terbium (Tb), “Q” is BeO, MgO, CaO, SrO, BaO, ZnO, Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, GeO<sub>2</sub>, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, or ThO<sub>2</sub>, “D” is vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), or nickel (Ni), “z” is 0 to 1, “u” is from 0 to 1, “y” is from 1 x 10<sup>-4</sup> to 0.1, “e” is from 0 to 1, and “t” is from 0 to 0.01.

10

16. The photothermographic material of claim 1 further comprising a phosphor that is a divalent alkaline earth metal fluorohalide phosphors characterized by the following formula (3):



15 wherein “M” is magnesium (Mg), calcium (Ca), strontium (Sr), or barium (Ba), “F” is fluoride, “X” is chloride (Cl) or bromide (Br), “I” is iodide, M<sup>a</sup> is sodium (Na), potassium (K), rubidium (Rb), or cesium (Cs), X<sup>a</sup> is fluoride (F), chloride (Cl), bromide (Br), or iodide (I), “A” is europium (Eu), cerium (Ce), samarium (Sm), or terbium (Tb), “z” is 0 to 1, “y” is from 1 x 10<sup>-4</sup> to 0.1, the sum of a, b and  
20 c is from 0 to 4, and r is from 10<sup>-6</sup> to 0.1.

25

17. The photothermographic material of claim 1 further comprising a phosphor and wherein said photosensitive silver halide and phosphor are in the same imaging layer.

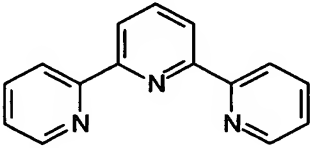
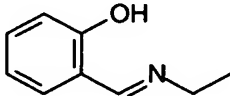
18. The photothermographic material of claim 1 comprising the same or a different imaging layer on both sides of said support.

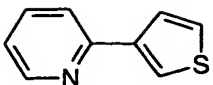
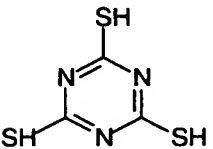
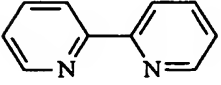
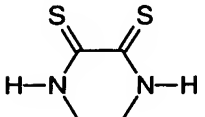
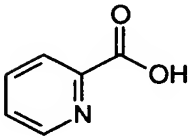
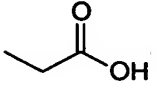
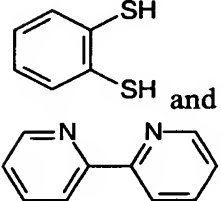
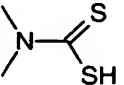
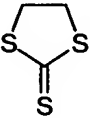
19. An X-radiation sensitive photothermographic material  
30 comprising a support having on at least one side thereof, a photothermographic

imaging layer having a dry coating weight of from about 5 to about 200 g/m<sup>2</sup>, and a surface protective layer, said imaging layer comprising a hydrophobic binder and in reactive association:

- a. a photosensitive silver bromide or silver iodobromide, or
  - 5 both,
  - b. a non-photosensitive source of reducible silver ions that includes silver behenate,
  - c. a reducing composition for said reducible silver ions comprising a hindered phenol or an ascorbic acid, and
  - 10 d. a phosphor that is sensitive to X-radiation and is present in an amount of from about 0.5 to about 20 mole per mole of total silver, the total silver present in said material being at least 0.002 mol/m<sup>2</sup>,
- said phosphor being one or more of YTaO<sub>4</sub>, YTaO<sub>4</sub>:Nb, Y(Sr)TaO<sub>4</sub>, and Y(Sr)TaO<sub>4</sub>:Nb,
- 15 said silver bromide or silver iodobromide grains having been chemically sensitized with a combination of chemical sensitizers that consists essentially of:
  - 1) one or more of the following gold (III)-containing compounds Au-1 to Au-14:

20

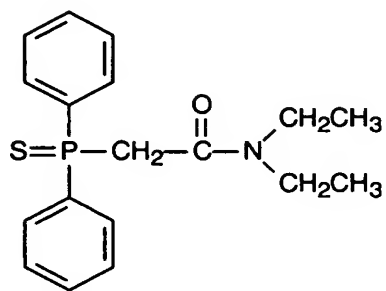
Compound	Au(III) Complex	Ligand-H (L'-H)
(Au-1)	AuL'ClBr <sub>2</sub>	P(phenyl) <sub>3</sub>
(Au-2)	AuL'Cl <sub>3</sub>	 <p>Terpyridine</p>
(Au-3)	AuL'Br <sub>2</sub>	

(Au-4)	$\text{AuL}'\text{Cl}_3$	
(Au-5)	$\text{L}'[\text{AuP}(\text{phenyl})_3]_3$	
(Au-6)	$\text{AuL}'\text{Cl}_3$	
(Au-7)	$\text{AuH}(\text{L}')_2\text{Cl}_2$	
(Au-8)	$\text{AuL}'\text{Cl}_2$	
(Au-9)	$\text{Au}_2\text{Zn}(\text{L}')_8$	
(Au-10)	$\text{AuPF}_6(\text{L}')_2$	
(Au-11)	$\text{Au}(\text{L}')_2\text{Br}$	
(Au-12)	$\text{AuL}'\text{Cl}_3$	
(Au-13)	$\text{Au}(\text{L}')_2(\text{ClO}_4)_3$	Diferrocenylphenylphosphine
(Au-14)	$\text{AuL}'\text{Cl}$	Glycylglycyl-L-histidine,

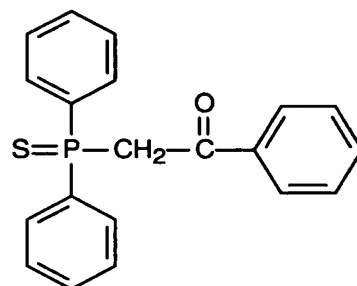
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and

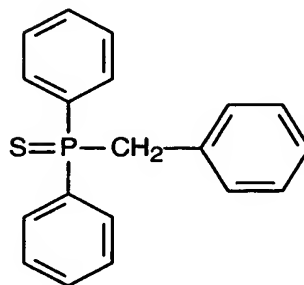
2) one or more of the following diphenylphosphine sulfide compounds PS-1 to PS-19:



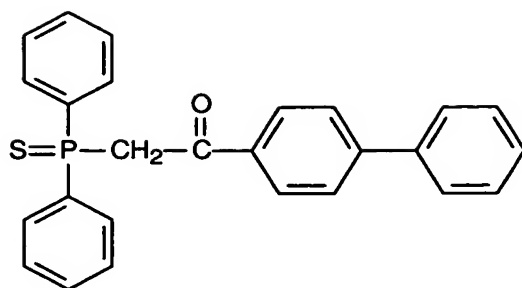
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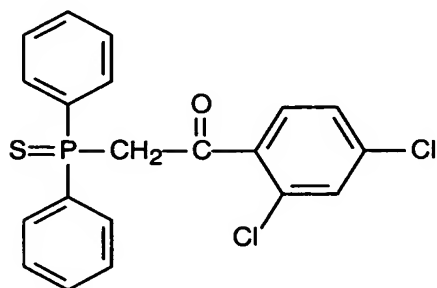
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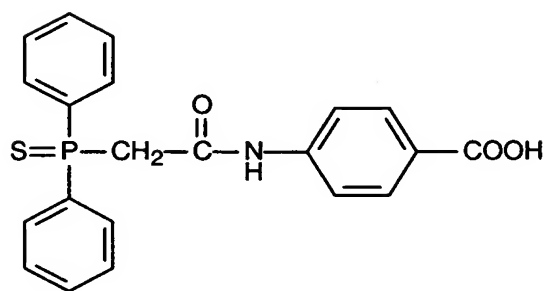
(PS-3)



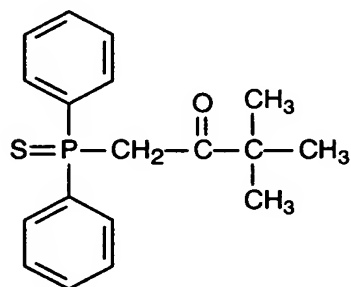
(PS-4)



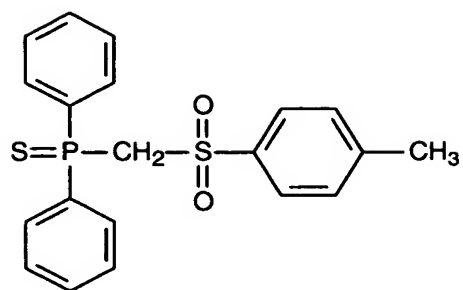
(PS-5)



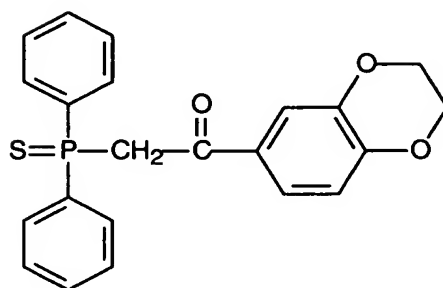
(PS-6)



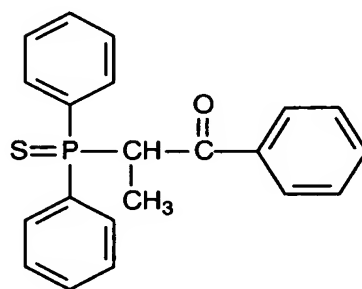
(PS-7)



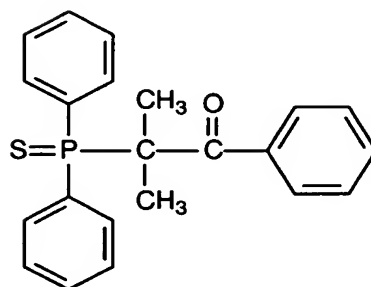
(PS-8)



(PS-9)



(PS-10)



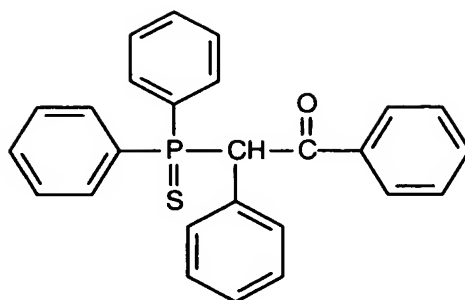
(PS-11)

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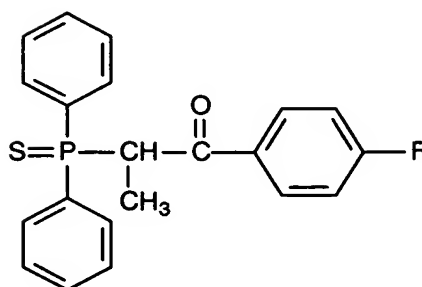
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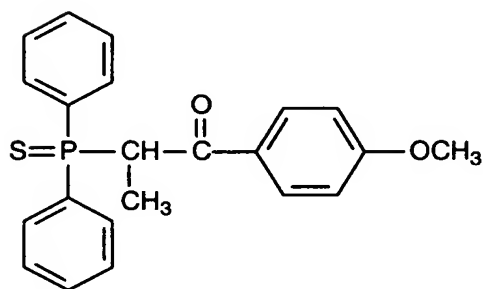




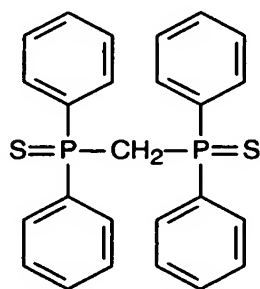
(PS-12)



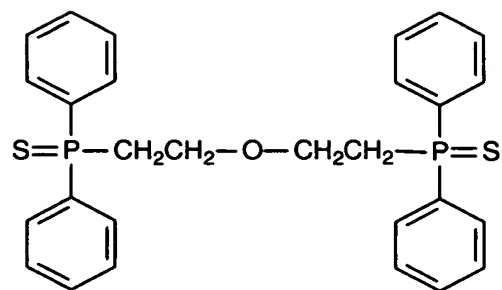
(PS-13)



(PS-14)

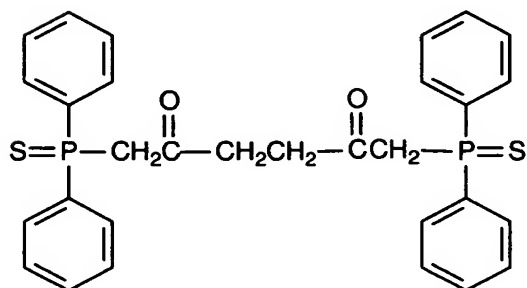


(PS-15)



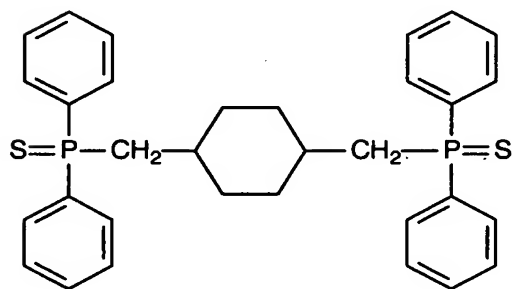
(PS-16)

5



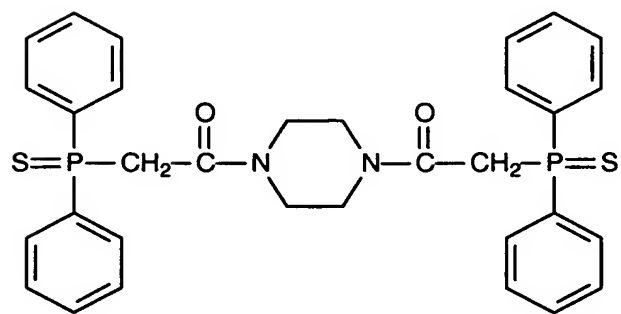
(PS-17)

10



(PS-18)

15



(PS-19).

the molar ratio of said gold(III)-containing compound to said diphenylphosphine sulfide compound used in the chemical sensitization is from about 1:1 to about 1:1,000.

5

20. The photothermographic material of claim 19 wherein said the same or different imaging layer is disposed on both sides of said support, with a protective layer disposed over each imaging layer.

10

21. A method for forming a visible image comprising:

A) imagewise exposing the photothermographic material of Claim 1 to electromagnetic radiation to form a latent image, and

B) simultaneously or sequentially, heating said exposed photothermographic material to develop said latent image into a visible image.

15

22. The method of claim 21 wherein said photothermographic material support is transparent, and said method further comprises:

C) positioning said exposed and heat-developed photothermographic material with a visible image therein between a source of imaging radiation and an imageable material that is sensitive to said imaging radiation, and

20

D) thereafter exposing said imageable material to said imaging radiation through said visible image in said exposed and heat-developed photothermographic material to provide a visible image in said imageable material.

25

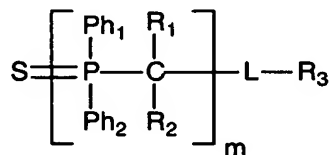
23. The method of claim 21 wherein said photothermographic material is X-radiation sensitive and is exposed to X-radiation to form said latent image.

24. A method of preparing a photothermographic emulsion comprising:

(A) providing a dispersion of a preformed photosensitive silver halide grains and a non-photosensitive source of reducible silver ions,

5 (B) providing one or more sulfur-containing compounds that is a diphenylphosphine sulfide compound, in association with said preformed silver halide grains and said non-photosensitive source of reducible silver ions, said diphenylphosphine sulfide compound being represented by the by the following Structure PS:

10



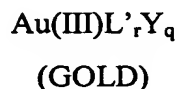
(PS)

wherein  $\text{Ph}_1$  and  $\text{Ph}_2$  are the same or different phenyl groups,  $\text{R}_1$  and  $\text{R}_2$  are  
15 independently hydrogen or an alkyl or phenyl group, L is a direct bond or a linking group, m is 1 or 2 and when m is 1,  $\text{R}_3$  is a monovalent group, and when m is 2,  $\text{R}_3$  is a divalent aliphatic linking group having 1 to 20 carbon, nitrogen, oxygen, and sulfur atoms in the chain,

(C) chemically sensitizing said preformed silver halide grains by  
20 decomposing said diphenylphosphine sulfide compound on or around said silver halide grains in an oxidizing environment to provide sulfur chemically sensitized photosensitive silver halide grains in reactive association with said non-photo-sensitive source of reducible silver ions, and

(D) providing a gold(III)-containing compound in association with said  
25 preformed silver halide grains and said non-photosensitive source of reducible silver ions to provide gold(III) chemically sensitized photosensitive silver halide grains in reactive association with said non-photosensitive source of reducible silver ions,

said gold(III)-containing compound represented by the following structure GOLD:



wherein L' represents the same or different ligands, each ligand comprising at least one heteroatom that is capable of forming a bond with gold, Y is an anion, r is an integer of from 1 to 8, and q is an integer of from 0 to 3,

the molar ratio of said gold(III)-containing compound to said sulfur-containing compound used in the chemical sensitization is at least 1:1..

25. The method of claim 24 wherein the molar ratio of said sulfur-containing compound to said gold(III)-containing compound is from about 5,000:1 to about 1:1, and said photosensitive silver halide grains are chemically sensitized with said sulfur-containing compound in an amount of from about  $10^{-6}$  to about  $10^{-1}$  mole per mole of total silver and with said gold(III)-containing compound in an amount of from about  $10^{-8}$  to about  $10^{-2}$  mole per mole of total silver.

26. The method of claim 24 wherein the steps are carried out in the order of step (A), step (B), step (C), and step (D).

27. The method of claim 24 wherein steps (B) and (D) are carried out simultaneously and before step (C).

28. The method of claim 24 wherein said diphenylphosphine sulfide compound is decomposed in an oxidizing environment.

29. The method of claim 28 wherein said oxidizing agent is a hydrobromic acid salt of an N-heterocyclic compound that is associated with a pair of bromine atoms.

30. The method of claim 24 wherein step (C) is carried out at a temperature of from about 10°C to about 30°C for up to 60 minutes.

5                    31. The method of claim 24 further comprising, after step (C), adding a spectral sensitizing dye to spectrally said photosensitive silver halide grains to from about 400 nm to about 1100 nm.

32. The method of claim 24 further comprising adding a  
10 reducing agent composition to said photothermographic emulsion.

33. The method of claim 24 further comprising:  
(E) converting some of the reducible silver ions in said non-photo-  
sensitive source of reducible silver ions to photosensitive silver halide.

15                    34. The method of claim 33 wherein the conversion of some of the reducible silver ions in said non-photosensitive source of reducible silver ions into photosensitive silver halide grains is carried out by one or more additions of an inorganic halide or an organic halogen containing compound.

20                    35. The method of claim 34 wherein said inorganic halide is selected from the group consisting of lithium bromide, calcium bromide, zinc bromide, and zinc iodide.

25                    36. The method of claim 33 wherein the steps are carried out in the order of step (A), step (B), step (C), step (D), and step (E).

37. The method of claim 24 wherein the steps are carried out in the order of step (A), step (B), step (D), and step (C).

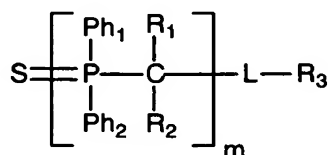
30

38. The method of claim 24 further comprising adding one or more phosphors to said photothermographic emulsion.

39. A method of preparing a photothermographic material  
5 comprising:

(A) providing a dispersion of preformed photosensitive silver halide grains and a non-photo-sensitive source of reducible silver ions,

(B) providing a sulfur-containing compound that is a diphenylphosphine sulfide compound in association with said preformed silver halide  
10 grains and said non-photosensitive source of reducible silver ions, said diphenylphosphine sulfide represented by the by the following Structure PS:



(PS)

15

wherein Ph<sub>1</sub> and Ph<sub>2</sub> are the same or different phenyl groups, R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an alkyl or phenyl group, L is a direct bond or a linking group, m is 1 or 2 and when m is 1, R<sub>3</sub> is a monovalent group, and when m is 2, R<sub>3</sub> is a divalent aliphatic linking group having 1 to 20 carbon, nitrogen, oxygen, and  
20 sulfur atoms in the chain,

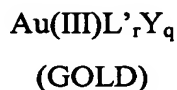
(C) chemically sensitizing said preformed silver halide grains by decomposing said diphenylphosphine sulfide compound on or around said silver halide grains in an oxidizing environment to provide sulfur chemically sensitized photosensitive silver halide grains in reactive association with said  
25 non-photosensitive source of reducible silver ions,

(D) providing a gold(III)-containing compound in association with said preformed silver halide grains and said non-photosensitive source of reducible silver ions to provide gold(III) chemically sensitized photosensitive silver halide

grains in reactive association with said non-photosensitive source of reducible silver ions,

said gold(III)-containing compound represented by the following structure GOLD:

5



wherein L' represents the same or different ligands, each ligand comprising at least one heteroatom that is capable of forming a bond with gold, Y is an anion, r is an integer of from 1 to 8, and q is an integer of from 0 to 3, and

(E') simultaneously with any of steps (B) through (D), or subsequently to step (D), adding a binder to form an emulsion formulation, and

(F) after step (E'), coating and drying said emulsion formulation on a support to provide a photothermographic imaging material.

40. The method of claim 39 wherein the steps are carried out in the order of step (A), step (B), step (C), step (D), step (E'), and step (F).

20 41. The method of claim 39 wherein steps (B) and (D) are carried out simultaneously.

42. The method of claim 39 wherein said diphenylphosphine sulfide compound is decomposed by the presence of a hydrobromic acid salt of a N-heterocyclic compound that is associated with a pair of bromine atoms.

43. The method of claim 39 further comprising, after step (C), adding a spectral sensitizing dye to spectrally said photosensitive silver halide grains to from about 400 nm to about 1100 nm

30

44. The method of claim 39 further comprising adding a reducing agent composition to said photothermographic emulsion, and



(E) converting some of the reducible silver ions in said non-photo-sensitive source of reducible silver ions into photosensitive silver halide grains by addition of an inorganic or an organic halide.

5                    45.     The method of claim 44 wherein said inorganic halide is selected from the group consisting of lithium bromide, calcium bromide, and zinc bromide.

10                   46.     The method of claim 44 wherein the steps are carried out in the order of step (A), step (B), step (C), step (D), step (E), step (E'), and step (F).

                    47.     The method of claim 39 wherein the steps are carried out in the order of step (A), step (B), step (D), step (C), step (E'), and step (F).

15                   48.     The method of claim 39 wherein the steps are carried out in the order of step (A), step (D), step (B), step (C), step (E), and step (F).

                    49.     The method of claim 39 further comprising adding one or more phosphors to said photothermographic emulsion.

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